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Abstract

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CATIONIC ACTIVITY OF THE COMPONENTS OF COMPLEX CATALYSTS

The metal halides of variable valence used in complex catalysts ($TiCl_4$, $ZrCl_4$, $FeCl_3$, etc.) prove to be very effective catalysts for the cationic polymerization of various monomers, as well as for such cationic processes as hydrocarbon isomerization and cis–trans isomerization of unsaturated compounds ([1–3]), etc. The halides of metals in their highest valence state possess the greatest cationic activity, while the reduced forms of these compounds possess the least.

The second component of complex catalysts is organic compounds of metals of groups I–III, among which the organometallic compounds of the alkali metals are well known as initiators of the process of anionic polymerization. Aluminum alkyls have found the widest use in complex systems. The anionic activity of trialkylaluminum is manifested in addition reactions of α-olefins, which proceed with the formation of products of the type

$$\mathrm{R{-}CH{-}CH_2{-}\overset{(+)}{\underset{\displaystyle R_1}{\underset{|}{Al}}}R_2}.$$

However, alkylaluminum halides already possess cationic activity, which increases in the series
$R_3Al < R_2AlHal < RAlHal_2 < AlHal_3$. Thus, monoalkylaluminum dichloride proves to be an effective catalyst for the polymerization of isobutylene and simple vinyl ethers at low temperatures ([4,5]). Alkylaluminum dichlorides are also catalysts for the hydrocarbon isomerization reaction and the Friedel–Crafts reaction ([6,7]). The cationic activity of dialkylaluminum halides is manifested in their ability to induce the polymerization of simple vinyl ethers ([8]), which, as is known, are most readily polymerized by a cationic mechanism. The study of the cationic activity of alkylaluminum compounds is of substantial interest for understanding the mechanism of action of complex catalysts and the nature of the secondary reactions that develop during polymerization under the influence of these systems.

The present work is devoted to the study of the cationic activity of dialkylaluminum chloride in the polymerization of various monomers (isoprene, isobutylene, butadiene, propylene, and styrene). The polymerization process was carried out in various solvents (benzene, toluene, hexane, and ethyl chloride) at temperatures from −78° to +20°C. In nonpolar solvents, dialkylaluminum chloride initiates the polymerization of the indicated monomers only in the presence of cocatalysts ordinarily used in cationic catalysis (water and acids), as shown for the polymerization of styrene (Table 1). The system under consideration is significantly more active in those cases where crystal hydrates of various salts and metal oxides are used as the cocatalyst. In this case the process is initiated on the surface of the crystal hydrate. A system consisting of R_2AlCl and crystal hydrates also induces the polymerization of isobutylene, isoprene, and butadiene (Table 1). Of the monomers studied, isobutylene polymerizes at the highest rate and butadiene at the lowest, which is in agreement with the relative activity of these monomers in the process of cationic

Table 1

Polymerization of various monomers in benzene solution under the action of R_2AlCl and various cocatalysts, $t = 20°$; R_2AlCl conc. 0.7–1.0% by weight of monomer; solvent : monomer ratio = 4 : 1 (vol.)

Monomer	Cocatalyst	Cocatalyst conc., g/10 ml solvent	Cocatalyst conc., mol/mol R_2AlCl	Duration of polymerization	Polymer yield, %	Unsaturation of polymer, % of theory	Polymer viscosity characteristic
Styrene	No additives	–	–	Polymerization does not occur	–	–	–
Styrene	H_2O	–	1	2 hours	15	–	–
Styrene	CH_3COOH	–	1	2 hours	10.0	–	–
Styrene	CH_3COOH	–	1	2 hours	12.7	–	–
Styrene	CH_3COOH	–	1	24 hours	12.3	–	–
Styrene	C_6H_5COOH	–	1	–	–	–	–
Styrene	$LiCl \cdot xH_2O$	1	–	10 min.	80	–	–
Styrene	$MgCl_2 \cdot xH_2O$	1	–	30 min.	100	–	–

Monomer	Cocatalyst	Cocatalyst conc., g/10 ml solvent	Cocatalyst conc., mol/mol R_2AlCl	Duration of polymerization	Polymer yield, %	Unsaturation of polymer, % of theory	Polymer viscosity characteristic
Isoprene	No cocatalyst	–	–	Does not polymerize	–	–	–
Isoprene	$LiCl \cdot xH_2O$	0.6	–	10 min.	23.5	52.7	0.418
Isoprene	$LiCl \cdot xH_2O$	0.6	–	15 min.	36.2	51.5	–
Isoprene	$LiCl \cdot xH_2O$	0.75	–	30 min.	43.5	53.0	–
Isoprene	$MgCl_2 \cdot xH_2O$	0.90	–	1 hour	15	59	–
Isoprene	$MgCl_2 \cdot xH_2O$	1.0	–	3 hours	32	54.6	–
Isoprene	$MgCl_2 \cdot xH_2O$	1.1	–	3 hours	35	50.6	–
Isoprene	$MgHPO_4 \cdot xH_2O$	0.9	–	36 hours	90	–	–
Isoprene	$MgSO_4 \cdot xH_2O$	0.9	–	6 hours	6	58	–
Isoprene	$Al_2O_3 \cdot xH_2O$	0.8	–	4 hours	12.7	61.4	0.26
Butadiene	No cocatalyst	–	–	Does not polymerize	–	–	–
Butadiene	$LiCl \cdot xH_2O$	0.2	–	24 hours	18.0	–	–
Butadiene	$LiCl \cdot xH_2O$	0.5	–	24 hours	31.5	40	–
Butadiene	$LiCl \cdot xH_2O$	0.7	–	24 hours	52.5	50.5	0.10
Butadiene	$BaCl_2 \cdot xH_2O$	0.8	–	–	31.5	57.5	–
Butadiene	$BaCl_2 \cdot xH_2O$	0.7	–	–	37.6	–	–

Monomer	Cocatalyst	Cocatalyst conc., g/10 ml solvent	Cocatalyst conc., mol/mol R_2AlCl	Duration of polymerization	Polymer yield, %	Unsaturation of polymer, % of theory	Polymer viscosity characteristic
Butadiene	$CaCl_2 \cdot xH_2O$	0.8	–	–	18.3	64.0	–
Isobutylene	No cocatalyst*	–	–	Does not polymerize	–	–	–
Isobutylene	$LiCl \cdot xH_2O$*	0.73	–	30 min.	50	–	–

* Polymerization in toluene solution at -78°.

polymerization. In the absence of dialkylaluminum chloride, the crystalline hydrates of these salts do not induce polymerization, just as dialkylaluminum chloride is inactive when thoroughly dried monomers and dehydrated salts or oxides are used. The diene polymers obtained with the indicated catalytic systems are characterized by reduced unsaturation (50-60% of theory), but are readily soluble in organic solvents. Trialkylaluminum, by itself or in the presence of the indicated cocatalysts, does not initiate polymerization. It is interesting to note that the process of cationic polymerization is inhibited in those cases in which a certain amount of trialkylaluminum is introduced into a system containing diethylaluminum chloride and a cocatalyst; as is known, trialkylaluminum belongs to the anion-active compounds.

The cationic activity of dialkylaluminum chloride increases sharply when ethyl chloride is used as the solvent. In this case the process proceeds in the absence of a specially introduced cocatalyst, whose role is apparently played by the solvent itself (ethyl chloride). Polymerization of isobutylene in ethyl chloride solution under the action of diethylaluminum chloride proceeds at a very high rate at a temperature of -78° and leads to the formation of polymers with a sufficiently high molecular weight (Table 2). Polymerization of butadiene at the same temperature proceeds, as might be expected, at a considerably lower rate,

Table 2

Polymerization and copolymerization of various monomers under the influence of R_2AlCl in ethyl chloride solution. $t = -78^\circ$; conc. R_2AlCl 0.3 mol. Solvent : monomer ratio = 4 : 1 (by volume)

Monomer	Duration of polymerization	Polymer yield, %	$[\eta]$	Molecular weight of polymer*	Iodine number	Content in copolymer of unsaturated units based on butadiene
Isobutylene	15 min.	20.6	1.02	247200		
Isobutylene	15 min.	100.0	0.73	148000		
Isobutylene	30 min.	26.3	1.09	274200		
Isobutylene	10 min.	52.5	1.65	524800		
Butadiene	16 h	10	–	–	318 **	
Butadiene	46 h	26				
Isobutylene + butadiene 90 : 100 (mol)	4 min.	65			8.9	1.89
Isobutylene + butadiene 90 : 100 (mol)	18 h 45 min.	47.5	0.46	–	11	2.3
Isobutylene + butadiene 50 : 50 (mol)	5 h 20 min.	11.5			16.8	3.56
Isobutylene + butadiene 50 : 50 (mol)	22 h	10.4			22.6	4.8

* The molecular weight of polyisobutylene was calculated from equation (9) $[\eta] = 2.6 \cdot 10^{-4} M^{0.61}$.

** Structure of polybutadiene (according to IR data): 13% of 1-2 units; 52% of

1-4 trans units.

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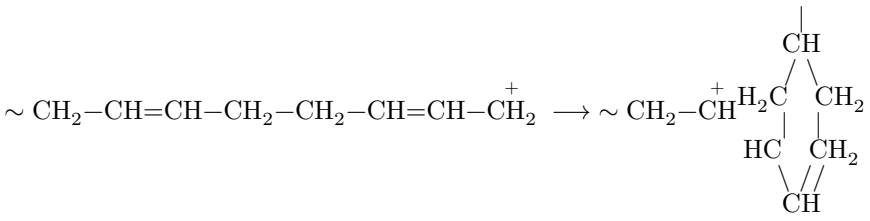
with the formation of a powdery amorphous polymer with a softening temperature of about 80° and an unsaturation of 67%.

In the copolymerization of a mixture of equimolecular amounts of butadiene and isobutylene, at a low degree of conversion the copolymer contains only about 7 mol.% of butadiene units, which is associated with the large differences in the copolymerization constants of the indicated monomers in cationic polymerization. Naturally, with increasing degree of polymerization the average content of butadiene units in the polymer increases. Dialkylaluminum chloride in ethyl chloride solution causes, at a temperature of about 0°, rapid polymerization of propylene with the formation of oily products with a molecular weight of about 1000. It should be noted that introduction of trialkylaluminum into the system, also in the case of polymerization in ethyl chloride, leads to complete inhibition of the process.

The strong decrease in the unsaturation of the copolymer in the cationic polymerization of dienes is associated with the development of secondary reactions in the polymer chain involving internal and external double bonds. These secondary reactions are most typical of the cationic mechanism, since attack by the cation is always directed at the site of greatest electron density. In the course of polymerization, interaction of the active center (the growing polymer cation) with a double bond of its own chain leads to the formation of lateral cyclic branches, and the resulting polymer, despite its greatly reduced unsaturation, retains the ability to dissolve in organic solvents. Such a chain may apparently have the following structure:



It should be expected that in cationic polymerization the nature of the counterion will play a substantial role, by analogy with the known role of the counterion in anionic polymerization. The possibility is not excluded,

that by changing the nature of the counterion (anion) one will be able substantially to alter the activity and selectivity of the system' s action, which, in particular, in the polymerization of dienes may lead to a change in the structure of the chain and to the elimination of the indicated secondary reactions.

Using the generally accepted ideas concerning the mechanism of action of cocatalysts in cationic polymerization, the mechanism of action of the systems under consideration may be represented through the stage of formation of an ion pair:

$$R_2AlCl + HOH \rightarrow [R_2AlCl \cdot OH]^{(-)}H^{(+)}$$

$$R_2AlCl + C_2H_5Cl \rightarrow [R_2AlCl_2]^{(-)}C_2H_5^{(+)}$$

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Note: Figure translations are in progress. See original paper for figures.